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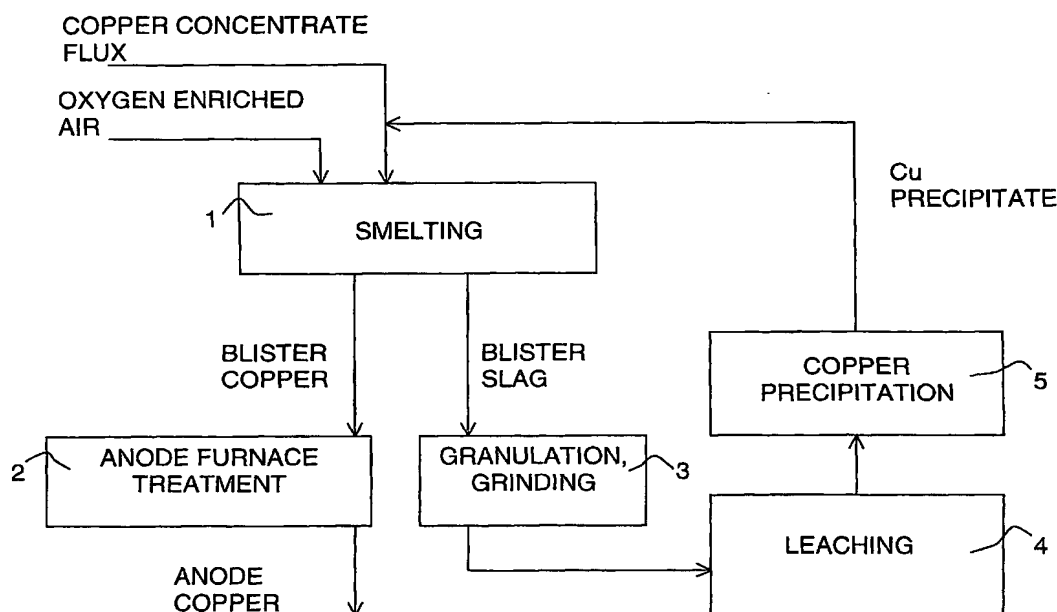
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(54) Title: METHOD FOR TREATING SLAG



(57) Abstract: The invention relates to a method for treating slag created in the production of blister copper processed directly from concentrate in a suspension smelting furnace, such as a flash smelting furnace, in order to recover the copper, so that at least part of the slag is leached in at least one step.

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METHOD FOR TREATING SLAG

The invention relates to a method defined in the preamble of claim 1 for treating the slag created in the production of blister copper.

The production of blister copper of sulfidic concentrates directly in one step in a suspension reactor, such as a flash smelting furnace, is economically sensible, with certain boundary conditions. Among the most remarkable problems in the direct production of blister copper are the slagging of copper and the created large quantities of slag. In order to ensure a sufficient recovery of copper, the amount of copper in slag must be recovered in connection with the slag cleaning. Apart from the quantity of slag, another problem is the large heat amount created in the combustion of sulfidic concentrates. In that case, there is applied a lower oxygen enrichment in the process air, which means that the heating of the nitrogen contained in the process air balances the heat economy. However, this produces a large quantity of process gases, which again results in a large furnace space and above all in large gas processing units.

In case the copper content of the concentrate is sufficiently high, typically at least 37% Cu, the production of blister is economically possible directly in one step. The thermal value of the concentrate is generally the lower, the higher is the copper content of the concentrate. With a high copper content, the share of iron sulfide minerals is low. When processing the above described concentrate, a sufficiently high oxygen enrichment can be used, and as a result, the gas quantities can be kept moderate. Also a concentrate with a lower copper content is suited in the production of blister copper, if it has a low iron content, in which case the created slag quantity is not remarkably large.

From the Finnish patent application 982818, there is known a method for producing blister copper, in which method in a smelting reactor there is conducted, in addition to the concentrate, also cooled and ground copper matte. Now there is created a smaller quantity of slag in proportion to the

quantity of produced blister copper than with the traditional method. Now also copper losses in slag are reduced. The created slags are processed further either in a one-step or preferably a two-step slag cleaning process. A two-step slag cleaning method includes either two electric furnaces or an electric furnace and a slag concentration plant. In the electric furnace, the slag is reduced by coke, so that the precious metals bound in the slag phase are reduced and separated as a distinctive copper phase underneath the slag layer. In case the slags are processed in a slag concentration plant, the slag concentrate can be fed back into the smelting reactor. The blister copper is conducted to be refined in an anode furnace.

If the slag is processed in one step in an electric furnace, so that the quantity of copper in the slag is economically insignificant, the iron content in the blister is still so high that there is often needed a separate treatment for the blister in a converter. One method is electric furnace pretreatment, where the created blister copper is processed together with bulk blister in an anode furnace, but there is still left so much copper in the slag that it must for economical reasons be recovered by concentration-technical means.

The object of the invention is to introduce a new method for treating slag created in the production of blister copper produced directly of concentrate. A particular object of the invention is to achieve a more effective and more advantageous way, with respect to overall economy, for recovering the slagging copper in the production of blister copper.

The invention is characterized by what is set forth in the characterizing part of claim 1. Other preferred embodiments of the invention are characterized by what is set forth in the rest of the claims.

The method according to the invention has many advantages. According to the method, there is advantageously recovered the copper contained in the slag created in the production of blister copper that is produced directly of

concentrate. The method of the invention simplifies the recovery of copper, and in addition, the method enables an improved control of impurities. The recovery of copper contained in hydrometallurgical slag reduces energy consumption in comparison with electric furnace reduction. In addition, gas and dust emissions are reduced in comparison with pyrometallurgical recovery.

The invention is described in more detail below with reference to the appended drawing.

Figure 1 Diagram of a process according to the invention

Figure 1 illustrates a method according to the invention for processing the slag, i.e. blister slag, created in the production of blister copper produced in a suspension smelting furnace, such as a flash smelting furnace, in order to recover the copper, in which case at least part of the slag is leached in at least one step. Copper concentrate, flux and oxygen enriched air are fed into smelting 1 in a suspension smelting furnace, such as a flash smelting furnace. Dried concentrate particles react swiftly in hot suspension with oxygen enriched air. Energy that is released in the reactions is utilized in the process. Part of the sulfur is oxidized into sulfur dioxide, and iron is oxidized into iron oxides, thus creating slag with the flux. The reaction products are settled on the bottom of the suspension smelting furnace creating two separate molten phases: blister copper and blister slag. The gases created in the process are conducted further, to be processed in a known fashion. The blister copper created in the suspension smelting furnace is conducted into anode furnace treatment 2, refined there in a known fashion and cast into copper anodes.

The blister slag created in smelting 1 is tapped out of the suspension smelting furnace through the provided circulation channels, such as launders, and is further conducted to be treated in order to recover the copper contained in the blister slag. First the blister slag is transferred to granulation and grinding 3. Granulated blister slag is ground for example in wet grinding down to a given

grain size in order to obtain more reactive surface. In leaching 4, the metals contained in the blister slag are leached. According to the example below, the leaching 4 is carried out in oxidizing conditions with sulfuric acid, so that copper sulfate is created. The amount of added sulfuric acid is advantageously 500 – 900 grams per one kilo of slag. The leaching can also be carried out by an ammoniacal solution, a chloridic solution or as bacteria leaching. After the leaching step, from the solution containing metal sulfates, copper is separated in copper precipitation 5. In the precipitation step, from the solution containing metal sulfates, copper is precipitated for example by hydroxide precipitation or sulfide precipitation. In hydroxide precipitation, copper is precipitated by limestone, and the created copper-bearing precipitate is conducted back to smelting 1. In sulfide precipitation, copper is precipitated by hydrogen sulfide, and the created copper-bearing precipitate is conducted back to smelting 1. Copper can also be recovered in liquid-liquid extraction and electrolysis as cathode copper.

EXAMPLE

In order to verify the method, there were carried out solution experiments with sulfuric acid in an acid-proof two-liter reactor with a lid. The reactor was provided with four flow baffling plates, one reflux condenser and an agitator. In the reactor, there was also connected continuous pH-measuring, a temperature regulator and oxygen bubbling underneath the agitator blades. A heat plate was used for heating.

At the beginning of the experiment, the slag (200 g = grams) was leached into water, the water quantity being a little less than a liter. In all experiments, the total volume of water and added sulfuric acid was exactly one liter. The solution temperature was 90° C. The quantity of sulfuric acid (H_2SO_4) that was added in the experiment was 806 g/1000 g slag.

The leaching period in all experiments was 6 hours, and mechanical agitation was applied in the experiments (about 770 r/min = rotations/minute) as well as oxygen (0.50 l/min = liters/minute).

Strong sulfuric acid (content 95% by weight) was gradually added, and at the same time the temperature was adjusted to 90° C. The measurement of the reaction time was started when all acid had been supplied. Slurry samples were taken when 0, 2, 4 and 6 hours had passed from the beginning of the experiment. In the filtrate and precipitate of the sample, there were analyzed copper (Cu) and iron (Fe).

Originally the leached slag contained 32.5% Cu and 23.9% Fe. The analyses and the leaching yields obtained on the basis thereof are given in the table below:

Time	Solution			Precipitate		Cu yield into solution
	pH	Cu, g/l	Fe, g/l	Cu, %	Fe, %	
0 h	0.5	59.8	16.8	8.8	23.6	72.6
2 h	1.1	80.0	22.4	4.1	25.7	88.3
4 h	1.2	82.0	23.6	3.4	23.6	89.4
6 h	1.2	87.0	24.6	3.1	23.8	90.4

The weight of the final precipitate was 77.4 g and copper content 3.1%, which means that the total copper yield in the solution was 96.3%.

The experiment was repeated in similar conditions for slag that was, instead of slow cooling, granulated by water directly from the molten state, so that the obtained product was finely divided granule with a corresponding composition. The obtained total leaching yield for copper in similar conditions was 95.8%, which is of the same order as with slowly cooled slag, when the accuracy of the analysis is taken into account.

From the solution, copper was precipitated selectively by adjusting acidity, so that iron was precipitated in the first step and copper in the second step, and thus the non-desired iron could be separated from the copper.

For a man skilled in the art it is obvious that the various preferred embodiments of the invention are not restricted to the above examples only, but may vary within the appended claims.

CLAIMS

1. A method for treating slag created in the production of blister copper processed directly from concentrate in a suspension smelting furnace, such as a flash smelting furnace, in order to recover the copper, **characterized** in that at least part of the slag is leached in at least one step.
2. A method according to claim 1, **characterized** in that the slag is granulated and ground before leaching.
3. A method according to claim 1 or 2, **characterized** in that the leaching is carried out with sulfuric acid.
4. A method according to claim 1 or 2, **characterized** in that the leaching is carried out with an ammoniacal solution.
5. A method according to claim 1 or 2, **characterized** in that the leaching is carried out with a chloridic solution.
6. A method according to claim 1 or 2, **characterized** in that the leaching is carried out as a bacteria solution.
7. A method according to any of the preceding claims, **characterized** in that after leaching, the copper is recovered by hydroxide precipitation.
8. A method according to claim 1 – 6, **characterized** in that after leaching, the copper is recovered by sulfide precipitation.
9. A method according to claim 1 – 6, **characterized** in that after leaching, the copper is recovered in liquid-liquid extraction and electrolysis as cathode copper.

10. A method according to claim 7 or 8, **characterized** in that the copper-bearing slag created in precipitation is conducted back into the suspension smelting furnace.

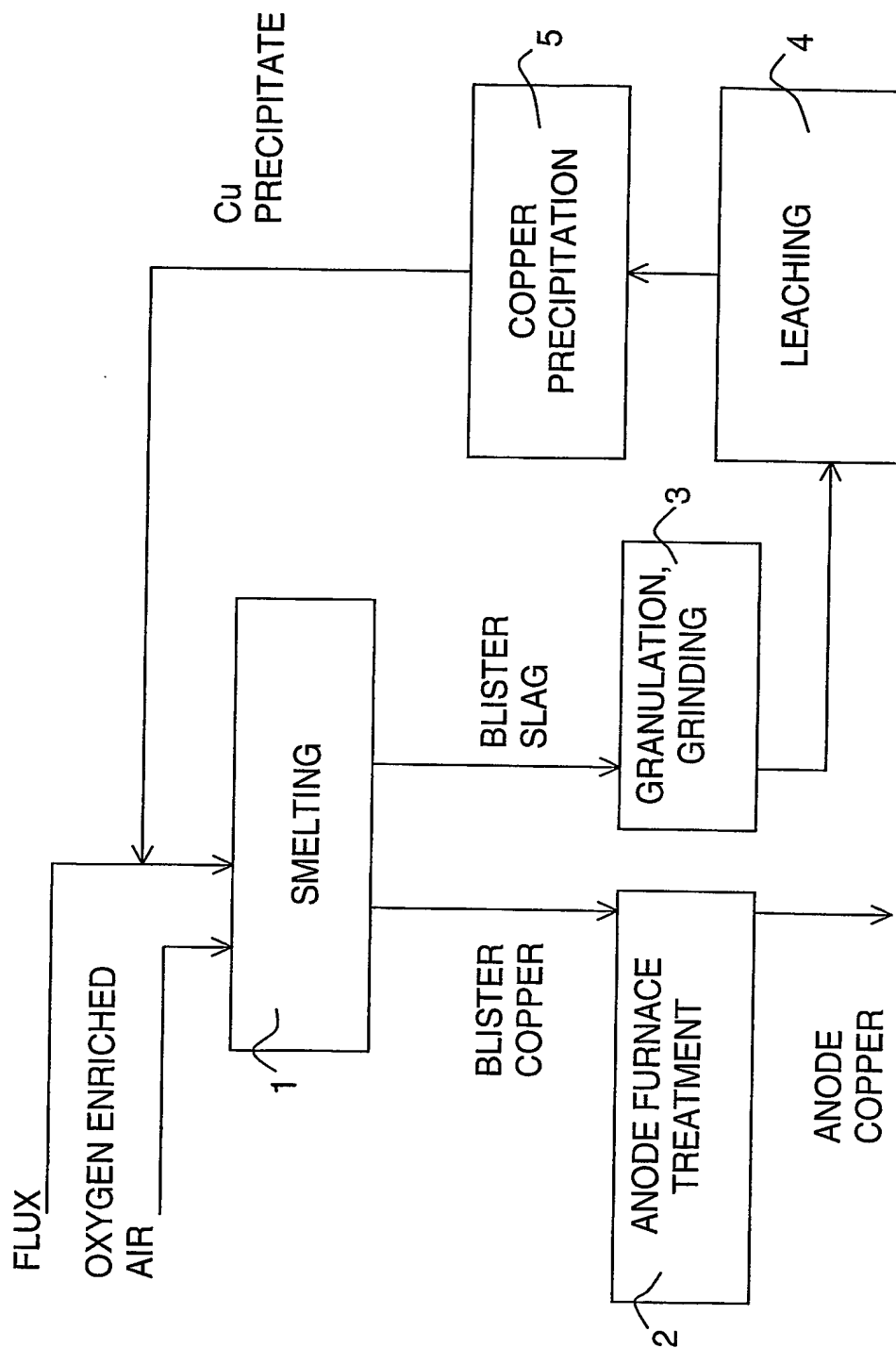


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2003/000898

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3632308 A (LAWRENCE C. KLEIN ET AL), 4 January 1972 (04.01.1972), column 1, line 24 - line 31, abstract --	1-3
X	DE 2348005 A (ALBRIGHT & WILSON LTD.), 25 July 1974 (25.07.1974), page 2, line 19 - line 28; page 3, line 7 - line 13; page 3, line 19 - line 25 --	1,4
P,X	CA 2363969 A1 (CURLOOK, WALTER ET AL), 26 May 2003 (26.05.2003), figure 2, abstract --	1,3

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International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4484730 A (ISSAY M. DIMITROV ET AL), 27 November 1984 (27.11.1984), column 1, line 37 - line 41; column 1, line 59 - line 61, abstract --	1-10
A	WO 0149890 A1 (OUTOKUMPU OYJ), 12 July 2001 (12.07.2001), figures 1,2 -- -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

24/12/2003

International application No.

PCT/FI 2003/000898

US	3632308	A	04/01/1972	NONE		
DE	2348005	A	25/07/1974	FR	2200200 A,B	19/04/1974
				IT	999580 B	10/03/1976
CA	2363969	A1	26/05/2003	NONE		
US	4484730	A	27/11/1984	NONE		
WO	0149890	A1	12/07/2001	AU	2112500 A	16/07/2001
				BR	0016890 A	08/10/2002
				CA	2395995 A	12/07/2001
				EA	3759 B	00/00/0000
				EP	1257676 A	20/11/2002
				FI	104838 B	00/00/0000
				FI	982818 D	00/00/0000
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